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Degradation of abiotically aged LDPE films containing pro-oxidant by bacterial consortium

P.K. Roy [a,*], S. Titus [b], P. Surekha [a], E. Tulsi [b], C. Deshmukh [b], C. Rajagopal [a]

[a] Centre for Fire, Explosive and Environment Safety, Timarpur, Delhi 110054, India
[b] Naval Material Research Laboratory, Shil Badlapur Road, P.O. Anand Nagar, Addl., Ambernath 421506, India

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ABSTRACT

The degradation of abiotically aged low density polyethylene (LDPE) films containing trace quantities of a representative pro-oxidant (cobalt stearate) was investigated in the presence of well defined enriched microbial strains namely, *Bacillus pumilus*, *Bacillus halodenitrificans* and *Bacillus cereus* in Basal salt medium. The films were initially subjected to an abiotic treatment comprising UV-B irradiation, and subsequently inoculated with the bacterial strains. The degradation in the polymeric chain was monitored by changes in the mechanical, morphological, structural and thermal properties. The abiotic treatment led to the formation of extractable oxygenated compounds as well as unoxidised low molecular weight hydrocarbons, which was confirmed by GC–MS studies. These were utilized by the bacterial consortium in the subsequent biotic phase and led to a mass loss of the polymer ($8.4 \pm 1.37\%$), which was also accompanied by an increase in the bacterial count. A decrease in the surface tension of the cell free medium was observed, which indicates that the bacterial consortium produced extracellular surface active molecules in order to enhance the bioavailability of the polymeric fixed carbon. The spectroscopic investigations reveal that the bacteria preferentially consume the oxygenated products leading to a decrease in the Carbonyl Index (CI), which in turn leads to an increase in the initial decomposition temperature as observed in the TGA traces. The morphological investigations reveal a biofilm formation on the surface, which was found to be scattered in certain regions and not uniform on the polymeric surface.

1. Introduction

Polyethylene, particularly as thin films, has found widespread use as a packaging material primarily because of its excellent mechanical properties, barrier properties against water borne microorganisms, low cost and high energy effectiveness [1]. However, this property of recalcitrance to microorganisms, which had once made polyethylene a popular choice as a packaging material, has now made it a subject of much criticism. Most of the polyethylene, after serving its useful life as a packaging film, finds its way to the landfill sites, where it simply refuses to degrade because of its non-biodegradable nature. The inherent resistance of polyethylene to biological attack can be attributed to its hydrophobic nature (carbon-only backbone), high molecular weight and the absence of functional groups recognizable by microbes. The major strategy to facilitate the disintegration and subsequent degradation of the polymeric polyethylene chain is focused on direct incorporation of carbonyl groups within the backbone or its in situ generation by introduction of pro-oxidant at the processing stage. Typical pro-oxidants include UV activators like aromatic ketones and/or transition metal based complexes.

Abiotic degradation in the presence of pro-oxidants generally leads to the formation of functional macromolecules, which can thermally or photochemically cleave repeatedly to low molecular weight oxygenated fragments. These include aliphatic carboxylic acids, alcohols, aldehydes and ketones which can support microbial growth and in turn get consumed by microorganisms [2,3].

There have been some studies on the biodegradation of pro-oxidant activated polyethylene in soil, wastewater, sludge and compost [4–6]. This approach offers several advantages, like diverse microbial inoculum or close relation to the real conditions in the nature and in waste treatment processes. However, very few studies have been carried out under controlled conditions, i.e. experiments with well identified strains in the medium.

As a part of our ongoing efforts in the development of degradable polyethylene [7–9], we report an investigation aimed at microbial degradation study of photodegraded LDPE.

* Corresponding author. Tel.: +91 11 23907282.
E-mail address: pk_roy2000@yahoo.com (P.K. Roy).

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2. Experimental

2.1. Materials

Cobalt acetate, sodium hydroxide, and stearic acid, ('AR' grade E.Merck) were used without further purification. General purpose film grade 'LDPE 24FS040' has been used to prepare films. Milli Q ultrapure water was used throughout the course of this work.

2.2. Film preparation

Cobalt stearate was synthesised by the reaction of cobalt acetate with sodium stearate according to the procedure reported in the literature [10]. The detailed procedure along with complete characterization of the pro-oxidant has been reported in our previous papers [7].

70 ± 2 μ films of LDPE were prepared by mixing 0.1% w/w cobalt stearate with LDPE in an extruder (Dayal make) with a 19 mm screw of L:D:22:1 attached to a film blowing die. An annular die with a diameter of 2″ and a die gap of 1 mm was employed for this purpose. Films of uniform thickness were prepared by maintaining a constant nip roller take up speed of 35 rpm under constant blowing. The temperature in the extruder was maintained at 120 °C (feed zone), 130 °C (compression zone) and 135 °C (die section). The photodegradable films prepared in this manner have been referred to as PLD in the text subsequently.

2.3. Abiotic treatment: photodegradation procedure

Seventy micrometer blown films of PLD were irradiated with four 40 W UV-B lamps generating energy between 280 nm and 370 nm with a λ_{max} at 313 nm. The spectral irradiance of the UV lamps has been depicted elsewhere [8]. Films were mounted on racks positioned 5 cm from the lamps and removed at regular intervals to monitor the level of degradation.

$$\text{Carbonyl Index (CI)} = \frac{\text{Absorption at } 1740\ \text{cm}^{-1}\ \text{(the maximum of carbonyl peak)}}{\text{Absorption at } 1460\ \text{cm}^{-1}\ \text{(internal thickness band)}}$$

2.4. Biotic treatment

2.4.1. Strains of bacteria

A consortium of three bacteria (*Bacillus pumilus*, *Bacillus halodenitrificans* and *Bacillus cereus*) was employed for the biodegradation of UV-irradiated samples. This consortium was developed by the enrichment of environmental bacteria in a liquid nutrient medium containing polyethylene as the sole source of carbon. This was done for a period of 20–24 months so as to allow the microbes to adapt to this carbon source and to enrich polyethylene degrading bacteria. Bacillus and its various species have been reported to play an important role in environmental biodegradation [11–13]. However, its efficacy for biodegradation of polyethylene has not been reported previously.

2.4.2. Medium and conditions for the cultivation of bacteria

The mineral medium utilized for the growth of bacteria contained (g^{-1}), NH_4Cl 1.0; K_2HPO_4 1.0; KH_2PO_4 0.5; NaCl 30; $MgSO_4 \cdot 7H_2O$ 0.5; $CaCl_2 \cdot 2H_2O$ 0.2; KCl 0.3; $FeCl_2$ 0.01 and 1 ml of trace metal solution (prepared by adding the following in g^{-1} of distilled water: $FeCl_2$ 1.5; H_3BO_3 0.006; $MnCl_2$ 0.1; $CoCl_2$ 0.19; $ZnCl_2$ 0.07; $NiCl_2$ 0.024; $CuCl_2$ 0.002; Na_2MoO_4 0.036 and HCl (25%)) 10 ml. The pH of the medium was adjusted to 7.5 with 1 N NaOH and was sterilized by autoclaving for 15 min at 120 °C. The inoculum consisted of 3% (v/v) 24 h old bacterial culture grown in the same medium. The flasks containing the bacterial culture were maintained at 30 °C with continuous shaking in a rotary incubator shaker (120 rpm). Polyethylene films (5 cm × 1 cm) were first washed with ethanol, rinsed in sterile distilled water, and subsequently dried till constant weight and exposed to this bacterial culture medium. The films were removed at regular intervals for monitoring the changes brought about by bacterial action. A set of control experiments were performed in flasks containing the polyethylene films in Basal nutrient medium devoid of bacterial culture.

2.5. Monitoring of degradation: analytical characterization

2.5.1. Mechanical properties

The tensile tests were performed on test specimens according to ASTM 882-85 using a Materials testing machine (Model JRI-TT25). Films (10 cm × 1 cm) were subjected to a crosshead speed of 10 cm/min. The tests were undertaken at 20 °C and a relative humidity of 65%. Five samples were tested for each experiment and the average value has been reported.

2.5.2. Spectroscopic investigations

The structural changes in the film due to both abiotic and biotic exposures were investigated using FTIR spectroscopy. The FTIR spectra of films were recorded at regular intervals on a BIO-RAD (FTS-40) spectrophotometer. Carbonyl Index (CI), was used as a parameter to monitor the degree of degradation of polyethylene, and has been calculated according to the baseline method [14].

2.5.3. Ultrasonication

The extraction of degradation products resulting from the photo-oxidation of LDPE film samples (both in the presence and absence of pro-oxidant) was performed as per the procedure reported in the literature [15]. A total of 0.5 g of sample, cut into small pieces, was mixed with 10 ml chloroform in a 20 ml glass vial and ultrasonicated in a Branson 2210 apparatus for 2 h in a hot water bath held at 55 °C. The extract obtained was concentrated by total evaporation of solvent at room temperature. Afterwards 2 ml of chloroform was added and the extract was filtered through a 0.2 μm filter prior to analysis.

2.5.4. GC–MS

Identification of the degradation products extracted from both LDPE and PLD samples was performed by GC/MS (Bruker EM640S), using Helium as the carrier gas. The GC was equipped with HP 5MS (30 m × 0.25 mm ID, film thickness 0.25 μ) of medium polarity. The oven temperature was programmed for 40 °C for 3 min to 280 °C at 10 °C/min, then held at 4 min at 280 °C. The identification of some of the degradation products was established by comparison of their mass spectra with NST database and checked by comparison of the retention times with that of a standard sample. Others were identified only by comparison with NST database.

2.5.5. Thermal properties

The thermal behavior was investigated using a Perkin Elmer Diamond Simultaneous TGA–DTA–DSC under nitrogen atmosphere in the temperature range 50–500 °C at a constant heating rate of